

FINAL REPORT

**Removal of Perchlorate and Other
Contaminants from Groundwater at JPL**

A Pilot Study

By

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EXECUTIVE SUMMARY

A study funded by National Aeronautics and Space Administration (NASA) to demonstrate the removal of trichloroethylene (TCE), 1,2-dichloroethane (DCA), carbon tetrachloride (CCl_4) and perchlorate (ClO_4^-) from groundwater at Jet Propulsion Laboratory (JPL) has recently been completed by Calgon Carbon Corporation. Calgon Carbon successfully utilized its integrated granular activated carbon (GAC) and ISEP+™ treatment systems for the removal of the contaminants from ground water during the study conducted between September 15, 1998 - March 5, 1999. Results indicated that the organic contaminants were reduced to low levels and perchlorate in various inlet concentration levels (upto ~1200 ppb) was removed to non-detectable levels (<4 ppb) in treated water. In addition, the system was successful in removing other anionic species such as nitrate and sulfate from the groundwater to low levels in treated water, while producing minimal amounts of regeneration waste.

The integrated ISEP+™ system (comprising continuous ion exchange system (ISEP®) and perchlorate and nitrate destruction module (PNDM)) was successfully demonstrated for about 10 days. Perchlorate and nitrate present in regeneration waste from ISEP® were destroyed and substantial amounts of sulfate (exceeding 96%) was removed in the PNDM. The regenerant (brine), thus 'purified' in the PNDM, was recycled and was effective in regenerating the resin for the period of study. The overall process waste from the integrated ISEP+™ system for treating up to ~1200 ppb perchlorate was about 0.16%, based on the volume of feed water. Over one-half of a million gallons of ground water at the JPL site was successfully treated to produce a high quality water with non-detectable TCE, DCA and CCl_4 concentrations, non-detectable perchlorate (<4 ppb), low nitrate (<2 ppm) and sulfate (<2 ppm) concentrations.

Testing at various process conditions enabled Calgon Carbon to optimize each of the process units of the ISEP+™ system and confirm steady state operation. Sufficient operating data were obtained from this pilot study to design full-scale ISEP® system and to further develop the ISEP+™ integrated system for the complex treatment needs of JPL and other sites.

1.0 INTRODUCTION

Perchlorate and other anionic contaminants in ground water are effectively removed by ion-exchange, a process where contaminant anions are exchanged and replaced by an innocuous anion, typically chloride. Ion-exchange is one of the most effective methods for most ground water treatment applications due to its efficiency in removing contaminants present in varying concentrations at relatively low costs. Most of the ion-exchange resins manufactured are used for water treatment and ion-exchange resins have been treating drinking water for several years. Although ion-exchange technology is well-known, the effectiveness of an ion-exchange process depends, among other factors, on the operational configuration of the process. Key parameters that determine the efficiency and impact the economics of an ion-exchange process are treatment ratio and regeneration waste. Treatment ratio refers to the volume of feed water that can be treated before breakthrough of the contaminant(s) is obtained. Regeneration waste refers to the volume of waste generated by the ion-exchange process while regenerating the ion-exchange resin saturated with contaminants. An effective ion-exchange process is one that achieves high treatment ratios while producing low regeneration waste. Calgon Carbon's ISEP® system utilizes an effective ion-exchange process configuration that achieves high perchlorate treatment ratios while producing minimal waste.

Calgon Carbon utilized its patented multi-port ISEP® valve in developing an ion-exchange system for the removal of perchlorate and other anionic contaminants from ground water. The system bears similarity to Calgon Carbon's ISEP®-based system used commercially for the treatment of nitrate from drinking water. The two fundamental advantages of the ISEP® system are better utilization of the mass transfer zone* and continuous split-flow or counter-current* regeneration, which lead to high treatment ratios and low regeneration waste as compared to conventional ion-exchange processes using fixed bed systems. The ISEP® system involves sequential segmentation of the mass transfer zone where on a continuous basis, the loaded segment of the resin is removed from the 'top' of the mass transfer zone and regenerated

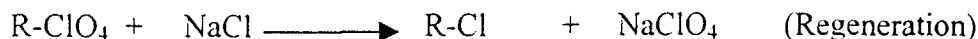
* The portion of the bed where ion exchange is taking place, sometimes called the "wavefront".

* 'Counter-current' in ISEP® refers to the fact that the direction of stream flow is opposite to the direction of rotation of the ISEP® columns.

resin is added back at the 'bottom' of the mass transfer zone, leading to better utilization of the ion-exchange resin during the adsorption cycle.

In the regeneration cycle, the technology utilizes a split-flow regeneration scheme where the regenerant flow is split equally and pumped into each column in the regeneration zone in parallel. This allows the fresh regenerant to be available to each column in the regeneration zone that results in efficient removal of perchlorate from the loaded resin compared to conventional fixed bed systems where split-flow regeneration is not feasible. This enables a highly efficient use of the regenerant thereby producing significantly lower wastes than the fixed-bed system. In another variation, regeneration of the resin in the ISEP® system may be accomplished by a staged counter-current mass transfer approach wherein the entire regeneration flow is passed through each column in series. In this configuration, the concentration of contaminants in the regenerant stream progressively increases as it traverses through each column in the regeneration zone. The resin columns, traveling in a direction counter-current (opposite) to the flow of regenerant, get progressively regenerated. This scheme can also result in an effective utilization of the regenerant, depending on the levels of contaminant loading on the resin. The ability to vary the configuration of adsorption and regeneration zones independently to operate at their optimum efficiencies on a continuous basis makes the ISEP®-based design effective, versatile and economical for ground water treatment applications involving ion-exchange.

Prior to the JPL pilot test program, Calgon Carbon had conducted extensive screening tests and identified an optimal anion exchange resin (Resorb+™) for the ISEP® system. The following scheme illustrates how perchlorate is removed by the ion exchange resin (R) in the ISEP® system:



The resin cycles through the above reaction steps in adsorption and regeneration zones of the ISEP® thus producing a continuous supply of treated water.

The ISEP+™ system piloted at JPL refers to ISEP® and a catalytic destruction and nanofiltration system together referred to as the perchlorate and nitrate destruction module

(PNDM). A granular activated carbon (GAC) system that serves to remove organic contaminants from the ground water prior to the ISEP® was also included in the pilot study. The PNDM serves to eliminate perchlorate, nitrate and sulfate from the spent brine stream from the ISEP®. The individual systems are further described in the following sections. For the purposes of this report, 'Integrated ISEP+™' refers to the fact that the individual components of the ISEP+™ (ISEP® and PNDM) are operationally integrated with each other.

2.0 ISEP+™ PILOT PROGRAM AT JPL

Calgon Carbon was retained by the Jet Propulsion Laboratory (JPL) to demonstrate the removal of organic contaminants (specifically, trichloroethylene (TCE), 1,2-dichloroethane (DCA) and carbon tetrachloride (CCl₄)) and inorganic anions (specifically, perchlorate) from the groundwater at its site. The pilot test program, conducted between September 15, 1998 and March 5, 1999, featured Calgon Carbon's ISEP+™ system, which was successful in removing all the target contaminants from the ground water. The program achieved major technological milestones in the removal and destruction of perchlorate from ground water, most notably the demonstration of an effective and efficient perchlorate and nitrate destruction system (PNDM).

2.1 Pilot Objectives

The original objectives for the program were revised by mutual agreement between Calgon Carbon and JPL. Revisions to the original objectives were necessitated by technological enhancements to the ISEP+™ system that rendered some of the original objectives obsolete or irrelevant to the main goals of the pilot study. The revised objectives for the JPL pilot study were:

- Determine the water chemistry of the source water at either the MW-7 or MW-16 site.
- Demonstrate treatment for the reduction of TCE, 1,2-DCA and CCl₄ to <5.0 ppb, <0.5 ppb and <0.5 ppb, respectively.
- Demonstrate removal of perchlorate to <4 ppb using the ISEP® unit.
- Demonstrate removal of nitrate in addition to removal of above contaminants.
- Optimize the individual process units of the ISEP+™ system and demonstrate continuous removal of the target contaminants in the integrated ISEP+™ system.
- Optimize the overall ISEP+™ system for the removal of all target contaminants while minimizing the volume of waste produced.

These objectives were achieved during the pilot program and salient results are presented in the report.

2.2 Technology Discussion

The conceptual diagram of the **ISEP+™** system as implemented at JPL is shown in Figure 1. The **ISEP+™** system is an integrated process system comprised of a granular activated carbon (**GAC**) system to remove the organic contaminants, a continuous countercurrent ion exchange system (**ISEP®**) for the removal of perchlorate, nitrate and other anions, and a **PNDM** system that contains a catalytic reactor system for destroying nitrate and perchlorate from brine plus a nanofiltration system to remove sulfate from brine. The **PNDM** system serves to purify the brine waste from **ISEP®**, thereby recycling the brine as regeneration feed for the **ISEP®** system.

In the process, the well water is passed through a granular activated carbon (**GAC**) system that serves to remove any organic contaminants in the water. Based on the data available from the JPL pilot study as well as an earlier pilot study, the **GAC** system has very limited perchlorate loading capacity in a ground water treatment system. Therefore, perchlorate breaks through rapidly from the **GAC** bed while the organics are retained. The organic-free well water is passed through the **ISEP®** system as indicated.

Depending upon pilot objectives, a perchlorate spiking system to spike the influent perchlorate concentration was used after the **GAC** system and prior to the **ISEP®** system. The **ISEP®** system contains thirty (30) columns attached to the rotating portion of the multi-port valve. Each of the columns is packed with the chloride form of the chosen anion-exchange resin. The **ISEP®** columns can be divided into three functional zones, namely, adsorption, regeneration and rinse. The perchlorate (as well as nitrate and sulfate) present in the feed water is exchanged with chloride on the resin in the adsorption zone. The water treated in this way by the columns in the adsorption zone can have non-detectable levels (< 4 ppb) of perchlorate. The resin containing adsorbed perchlorate is treated in the regeneration zone using a brine solution that exchanges the perchlorate, nitrate and sulfate ions on the resin with the chloride ions from brine. The regenerant for the JPL pilot study was designed to be a 7% NaCl solution (brine) prepared using softened city water. Even though the brine concentration in the regeneration zone was set at 7% NaCl, it was determined at the end of the study that the conductivity-based control in the brine feed tank intended to regulate the rich brine, fresh water and recycled brine flows to maintain 7%

NaCl did not function properly throughout the study. As a result, the actual concentrations of brine were lower and were between 2.5-4.5% NaCl throughout the pilot study. This does not affect the conclusions from the study and moreover, it has a positive impact on the performance of the ISEP® system. This is because regenerant consumption decreases with increasing concentration of brine. So, the waste percentages reported during the optimization of the ISEP® can be expected to be even lower when 7% NaCl is used.

The brine flow in the regeneration zone was initially operated in series flow counter current configuration* leading to sufficient concentration gradients between the brine phase and the resin phase in each column in the regeneration zone. For most of the treatment study, a split-flow regeneration configuration was implemented. This was accomplished by splitting the regenerant flow into each column of the regeneration zone. The advantage of this method, as mentioned in Section 1.0, is the availability of fresh brine to each column in the regeneration zone thereby achieving the highest regeneration efficiency in each column.

The spent brine effluent from the ISEP® regeneration zone understandably contains the perchlorate anions in a significantly higher concentration than the feed. The rinse zone serves to remove the entrained brine from the columns coming out of the regeneration zone before they enter the adsorption zone for the next cycle. The rinse flow effluent is a weak brine solution that is treated by the RO unit to produce a product and concentrate stream. The product stream is purified water which is used to make-up part of the rinse flow influent. The concentrate stream is a brine solution that is utilized to make-up fresh regenerant used in the regeneration zone. The columns cycle through adsorption, regeneration and rinse zones with controllable residence times in each zone. The residence time calculations for each zone is translated into step time, which indicates the time for which the columns (and the valve) stay in one position. The step time for the ISEP® system during the JPL pilot was set at 16.6 min. In other words, the 30-column ISEP® system took 8.3 hours to complete one rotation. The treated water from the ISEP® system was then sent to a GAC guard bed intended to capture any perchlorate leakage from the ISEP®, thereby discharging treated water with non-detectable levels of perchlorate. The treated

* See Section 1.0 for a description of the counter current staged mass transfer operation in the ISEP regeneration zone.

water from the **GAC** guard bed complied with regulatory requirements throughout the pilot study and showed non-detectable levels of perchlorate for most of the testing period.

The spent brine effluent from the **ISEP®** system is sent to a catalytic reactor system to which small amounts of a reductant (such as ethanol) is added. Perchlorate and nitrate present in the brine effluent are reduced to chloride and molecular nitrogen respectively, while the reductant is oxidized to carbon dioxide and water. This reduction-oxidation (*redox*) reaction occurs over a proprietary solid catalyst in the reactor at an elevated temperature and pressure. The effluent from the reactor is almost free of perchlorate and nitrate and is passed into a nanofiltration (NF) system where sulfate is removed from the brine into a small purge stream containing high concentrations of sulfate, but no perchlorate and nitrate. The purge stream from the NF system is the only waste stream from the entire process. This waste stream is expected to be in the range of 0.05-0.2% of the total feed water treated by the process. The product brine from the NF system is now 'purified' as it is free of perchlorate, nitrate and contains low levels of sulfate. This brine is recycled back into the regeneration zone of the **ISEP®** system along with a small fresh brine make-up stream. Thus, the entire brine treatment train is nearly a closed-loop process where more than 90% of the **ISEP®** brine effluent is recycled. Thus, the entire **ISEP+™** process results in effective removal of contaminants while producing minimal waste for disposal.

2.3 Program Methodology

The **ISEP+™** system described above was implemented in two phases. The first phase involved the demonstration and optimization of the **GAC** and **ISEP®** systems for removal of target organic and anionic contaminants. The second phase involved the demonstration and optimization of the **PNDM** system and the integration with **ISEP®** to demonstrate the integrated **ISEP+™** treatment system.

2.3.1 Pilot Optimization Methodology

Phase I: A dual-**GAC** bed was designed based on the influent concentrations of the organics and operated in series. As mentioned earlier, **GAC** has a limited capacity for perchlorate removal. Nevertheless, to avoid the perchlorate breakthrough profile from the **GAC** system and its temporary reduction of the influent concentration to the **ISEP®**, the **GAC** was pre-treated

with a dilute solution of ammonium perchlorate to saturate the **GAC** system with perchlorate. This was done to achieve the steady state **GAC** performance right from start-up, and thus efficiently utilize the pilot testing time towards optimizing **ISEP®** and **PNDM**.

It should be emphasized that **GAC** pre-treatment is neither advantageous nor required for commercial scale operation as the **GAC** effluent perchlorate concentration will reach that of the influent after a relatively short breakthrough period (~3-5 days). A schedule for **GAC** change-out was developed and implemented based on the organic leakage observed from the first bed. This proved sufficient to ensure the continuous removal of organics from the **GAC** system. The sampling points in the **GAC** system (influent, after first bed and just prior to the **ISEP®** system) were chosen so as to monitor organics removal performance and change-out **GAC** at appropriate frequencies.

The **ISEP®** system was first operated at design conditions (6% waste) to demonstrate removal of perchlorate and other anions. Then, optimization of the **ISEP®** followed at different inlet concentrations. Perchlorate concentrations of 250 ppb and ~1200 ppb were chosen to conduct the optimizations. The optimization program involved minimizing the brine effluent (or regenerant use) in the **ISEP®** system. After each change in the brine flow rate, the system performance was monitored for at least 2 days (approximately 6 rotations of **ISEP®** system) to determine the impact of the process change. After the final optimized brine flow rate level was reached, the **ISEP®** system was maintained at the optimal process conditions for the remainder of pilot test. During Phase I of the pilot test period, the spent brine was stored in a large waste tank and was periodically removed from the site and properly disposed by Safety-Kleen Corporation. The samples in the **ISEP®** were taken at the inlet and outlet of adsorption zone and the brine samples were taken from the rinse and regeneration zones. In addition, treated water samples were taken at five different columns evenly distributed within the adsorption zone. Samples were also taken after the guard **GAC** bed just prior to discharge from the site.

Phase II: This phase consisted of continued operation of the **ISEP®** at the optimal conditions for ~1200 ppb ClO_4 and treating the spent brine effluent by the **PNDM**. The spent brine was passed through the catalytic reactor system, where the performance of perchlorate and nitrate

destruction was demonstrated and contact time optimization study was conducted. In addition, the performance of the nanofiltration system was evaluated and fine tuning adjustments to obtain desired performance were made. Since optimization of the **ISEP®** and **PNDM** were independently conducted, the final step was to integrate all the unit operations to evaluate the performance of the integrated **ISEP+™** system. This was demonstrated towards the end of the pilot which marked the completion of the pilot program.

2.3.2 Sampling and Analytical Protocols

Sampling of various **ISEP®** and **PNDM** streams were conducted throughout the study. The **ISEP®** samples were taken over a period of one step time (16.6 min.) to remove the effect of intrastep concentration profiles thereby observing the true trends in the system. Samples taken from **PNDM** were typically grab samples and they were sufficient indicators of the true system performance. For anions analyses, the samples were collected in plastic bottles with solid screw cap covers. For organics analyses, the samples were collected in clear glass bottles with no headspace and covered by screw caps with teflon septa. In addition, samples collected for special analyses followed appropriate EPA protocols for sample collection, storage and analyses. Perchlorate and other anions were analyzed using two high-resolution ion chromatography systems, one customized to detect low-level perchlorate and the second for other anions. The analytical method used for perchlorate and other anions was the EPA method 300.0 (modified) for anions analyses. The samples containing high brine concentrations were pre-treated by a silver nitrate cartridge to minimize the interference of chloride on perchlorate analysis. Analyses of the organics were conducted using a gas chromatograph with an electrolytic conductivity detector.

3.0 RESULTS AND DISCUSSION

A representative profile of target organics and perchlorate observed in the groundwater from the MW-7 well site is shown in Figure 2. It is clear that perchlorate concentration from the well head fluctuated significantly and was in the range of 110-160 ppb for the majority of the test. Among the organics present in the well head, CCl₄ varied between 14-35 ppb and TCE between 6-15 ppb for the bulk of the test. Interestingly, the 1,2-DCA remained constant and at a very low level (< 0.5 ppb) throughout the test. The results obtained from performance evaluation and optimization studies of the individual process units of the ISEP+™ system are discussed below.

3.1 GAC System Performance

Representative steady state results showing removal of 1,2-DCA, CCl₄, TCE and over the GAC system are shown in Figures 3, 4 and 5 respectively. The 1,2-DCA inlet and outlet concentrations were both less than 0.5 ppb indicating that the impact of GAC on the reduction in 1,2-DCA could not be detected. On the other hand, the GAC system consistently removed CCl₄ and TCE down to less than 0.5 ppb in the treated water. The period of operation between GAC change-outs were designed to ensure that all the target organics are continuously removed to less than 1 ppb in treated water. It was mentioned earlier that activated carbon has a limited capacity for perchlorate in ground water. The pilot data collected at JPL (shown in Appendix) as well as at an earlier field test site indicated that the perchlorate breakthrough profile from a GAC bed continuously increases till it reaches the influent concentration and remains at that level. There was no evidence of perchlorate displacement from GAC bed. In other words, the perchlorate concentration at the effluent of the GAC system never exceeded the influent concentration.

3.2 ISEP® Performance and Optimization

After initial optimization of the rinse flow to ensure effective and efficient rinse of the resin coming off the regeneration zone, the bulk of ISEP® demonstration and optimization focused on minimizing the regenerant consumption (i.e., spent brine flow rate). The continuous removal of perchlorate from the influent water by the ISEP® system for two different inlet concentrations is

shown in Figure 6. It is evident that the ISEP® system produced near-complete removal of perchlorate at both inlet concentrations. At ~250 ppb inlet ClO_4 , the system was optimized to produce treated water with non-detectable perchlorate (< 4 ppb) concentration and a regeneration brine effluent (waste) of 1.25%, based on the volume of feed water. At the ~250 ppb perchlorate influent concentration level, the regeneration was conducted in series flow configuration. To obtain even higher regeneration efficiencies, the regeneration configuration was changed to split-flow before conducting performance and optimization studies at ~1200 ppb ClO_4 . Even at ~1200 ppb ClO_4 inlet, the system was effective in producing less than 4 ppb perchlorate in treated water for an optimized regeneration effluent level of 1.75%, based on feed water. It is important to note that a nearly five-fold increase in feed perchlorate concentration (from 250 ppb to 1200 ppb) was easily accommodated by only a 40% change in regenerant consumption. The ISEP® system, in this pilot study as well as in earlier studies, proved capable of handling feed waters of widely varying perchlorate concentrations, after only a minor adjustment to regenerant consumption. In all cases, the treated water produced contained non-detectable level of perchlorate at optimized conditions.

Small portions of the curve in Figure 6 where treated water perchlorate concentration significantly exceeded non-detectable levels is attributed to an inadvertent loss of regenerant flow to the ISEP® caused by malfunction of the regeneration feed pump. Once the regenerant flow was restored, the ISEP® performance was restored thereby producing non-detectable perchlorate in treated water, as shown in Figure 6. Nitrate removal performance was also temporarily affected by the impact of inadvertent loss of regenerant flow as shown in Figure 7.

In addition to perchlorate removal, the ISEP® system was effective in concomitantly removing substantial amounts of nitrate and sulfate from the feed water, as shown in Figures 7 and 8. About 90% of influent nitrate (15-20 ppm down to < 2 ppm) and more than 95% of the influent sulfate (from 45-50 ppm down to < 2 ppm) were removed from the inlet water. The treated water produced by the ISEP® system was of superior quality with the representative characteristics shown in Table 1.

The treated water from the ISEP® was sent to another GAC system (guard bed) and discharged from the GAC guard bed. This was done as an additional precaution to ensure that the treated water discharged complies with all federal, state and local regulations. The discharged water was periodically monitored throughout the pilot study and results indicated that the perchlorate level in the discharged water always remained below the California PAL (< 18 ppb) and remained at non-detectable (< 4 ppb) levels, for the most of the pilot study. A representative analytical profile of discharged treated water is shown in Table 1.

Table 1. Representative treated water characteristics produced at the outlet of the ISEP® system during the JPL pilot trial.

<i>Target Contaminant</i>	<i>Concentration</i>
ORGANICS:	
1,2-DCA	< 0.5 ppb
CCl ₄	< 0.5 ppb
TCE	< 0.5 ppb
ANIONS:	
Perchlorate	< 4 ppb
Nitrate	< 2 ppm
Sulfate	< 2 ppm

3.3 PNDM Performance and Optimization

The perchlorate and nitrate destruction module (PNDM) was brought on-line after successful optimization of the ISEP® system in treating feed water at ~ 1200 ppb ClO₄ to produce non-detectable perchlorate in treated water at a spent brine level of 1.75%. A typical composition of the spent brine is shown in Table 2. This spent brine effluent from the ISEP® was stored and used for performance evaluation and optimization of the PNDM. The catalytic reactor system was operated at different temperatures, pressures and contact times during the optimization study and their impact on perchlorate and nitrate destruction kinetics was ascertained.

Table 2. Typical anion composition of spent brine effluent from the ISEP® system, influent to the PNDM.

<i>Anion</i>	<i>Concentration</i>
Perchlorate	$\sim 60,000$ ppb
Nitrate	$\sim 1,000$ ppm
Sulfate	$\sim 3,500$ ppm

The catalytic reactor system in the **PNDM** is comprised of a fixed bed containing solid catalyst pellets, made from a proprietary composition. Although the exact mechanism of perchlorate and nitrate reduction is debatable, laboratory and pilot data indicated that both nitrate and perchlorate are reduced via intermediates that contain progressively lower oxidation states of nitrogen and chlorine respectively. The reaction occurring on the catalyst is reduction-oxidation (*redox*) where the slight stoichiometric excess of ethanol fed into the reactor is oxidized to carbon dioxide and water, concurrently reducing perchlorate and nitrate present in the brine stream to chloride and nitrogen, respectively.

Internal laboratory studies with the catalyst prior to the pilot study indicated that the reactions of perchlorate and nitrate reduction could each be categorized as first order* with respect to each of the reactants. In addition, nitrate destruction occurs more readily than perchlorate destruction over the catalyst. These results were borne out by pilot data as indicated below.

The steady state destruction of perchlorate achieved by the catalytic system during the pilot trial is shown in Figure 9. It is evident that perchlorate destruction exceeding 99.8% was achieved producing non-detectable (<125 ppb)[#] perchlorate concentration in brine. The kinetics of perchlorate destruction at the tested conditions followed first order with a reaction rate constant of 0.0013 sec⁻¹. Concurrently, nitrate present in the brine was also completely destroyed as shown in Figure 10. The treated brine from the reactor had a non-detectable (<20 ppm) nitrate concentration. Consistent with our laboratory studies, the rate constant for nitrate destruction in the pilot study was substantially higher than that for perchlorate destruction. Perchlorate and nitrate destruction are parallel reactions occurring on the catalyst surface.

The proprietary catalyst used for the pilot study, similar to many other catalysts, is subject to loss of activity (deactivation) under abnormal conditions. Deactivation can be either reversible or irreversible depending upon the phenomena causing it. Reversible deactivation in this treatment system is most commonly induced by loss of reductant flow in the treatment stream. In the

*Implies that the effluent concentration of the reactant decreases exponentially with reaction time.

[#] Due to interference by the high concentration of chloride ions in brine, the perchlorate detection limit in brine is 125 ppb as opposed to 4 ppb or less in water. Similarly, the nitrate detection limit in brine is 20 ppm as opposed to 0.2 ppm in water.

absence of the reductant (say, ethanol), the catalyst will be unable to reduce perchlorate and nitrate. Based on data obtained from the pilot study, such loss of activity is immediately restored when the reductant flow is re-established. In other words, the catalyst regains its original activity in the presence of reductant. Irreversible deactivation may occur by the deposition or interference of certain undesirable compounds (catalyst poisons) that may be present in the brine stream. Some compounds or elements that may poison the catalyst are iodine, organosulfur, organonitrogen, heavy metal (such as vanadium) compounds and to a lesser degree, iron. Poisoning of the catalyst to a level where the performance is substantially affected is known to occur primarily under sustained exposure to the poisons at significant concentration levels. Since these compounds are not normally present in most ground water streams, the catalyst is not likely to be poisoned under normal operating conditions. The reaction rate constant remained the same throughout the pilot study at JPL indicating that the catalyst was not poisoned and moreover, no potential catalyst poisons were detected in the water or brine streams.

The treated brine from the catalytic reactor was stored and used for evaluation of the nanofiltration (NF) system. The NF system consists of a membrane that separates divalent anions from monovalent anions. Thus, the divalent sulfate anions are selectively removed from the brine stream. Two parameters that describe the performance of the NF system are recovery and rejection rate. Recovery refers to the percent of feed that is recovered as permeate (or product) and rejection rate refers to the percent of target ion (sulfate) present in feed that is rejected to the waste (or concentrate) stream. Optimization of the nanofiltration system was conducted by varying the recovery of brine and studying its impact on sulfate rejection rate. Once an appropriate recovery was set, efforts to improve the quality of the recovered brine by varying the operating pressure were conducted. The impact of NF operating pressure on the quality (sulfate concentration) of permeate is shown in Figure 11. A slight improvement in permeate quality is obtained at increasing pressures which appeared to level off around 300 psig. The NF system was set to operate at 300 psig and produced a 91% brine recovery and a 96% sulfate rejection rate. This implies that only 9% of the inlet brine stream is discarded as the waste (concentrate) stream. This is the only waste stream produced in the ISEP+™ process. This waste stream corresponds to ~0.16% of the total feed water treated by the ISEP® system.

Moreover, this low waste stream primarily consists of sulfate in brine but non-detectable amounts of perchlorate or nitrate and so, can be easily disposed.

3.4 Overall Process (ISEP+™) Integration

Since the individual process units of the ISEP+™ system were independently validated and optimized, integration of the overall process was accomplished as the final requirement of the pilot study. The integration strategy followed is highlighted in Figure 12. First, the ISEP® system was continuously integrated with the catalytic reactor system. Next, the catalytic reactor system was integrated with the NF system. Finally, the permeate stream ('purified' brine) from the NF system was integrated with the ISEP® brine feed control tank. The automated level and conductivity controls in the brine feed tank instantaneously adjusted the rich brine and make-up water flows to ensure that the brine feed into the ISEP® remained at the design flow rate and concentration. The integrated ISEP+™ system operated continuously for about 10 days before the pilot was shutdown.

Results obtained from the integrated system indicated that the ISEP® continued to produce treated water below California PAL while using about 91% reclaimed or 'purified' brine. The overall process waste from the integrated ISEP+™ system was about 0.16%, based on the feed water influent to the system. Analysis of the process waste stream indicated that it had a sulfate concentration of about 2% in brine with no detectable amounts of perchlorate (<125 ppb) or nitrate (<20 ppm). While this performance is in line with the criteria for the successful integration of the entire system, it should be recognized that this performance is based on a relatively short duration (~10 days) of integrated operation. Calgon Carbon is presently conducting further developmental activities to better understand the potential issues that may arise in long term operation of the ISEP+™ system. It is anticipated that the developmental issues would be resolved and the integrated ISEP+™ system would be commercialized in the third quarter of 1999.

4.0 CONCLUSIONS

Calgon Carbon has successfully demonstrated its **GAC**, **ISEP®** and **PNDM** systems for the removal and/or destruction of organics, perchlorate, nitrate and sulfate present in the ground water at JPL. All of the revised pilot objectives, mentioned earlier, were accomplished during the pilot study. The results indicated effective removal of organics by the **GAC** system. The results clearly demonstrated that even at influent perchlorate levels of ~1200 ppb, the **ISEP®** system produced a treated water with non-detectable level of perchlorate at a relatively low regeneration (brine) effluent level of 1.75%. Concomitantly, substantial amounts of influent nitrate and sulfate were also removed. The **PNDM™** system was successful in achieving near-complete destruction of perchlorate and nitrate from the **ISEP®** spent brine effluent stream. The nanofiltration system was effective in producing substantial amounts of 'purified' brine, while maintaining a high sulfate rejection level. Based on the several performance evaluation and optimization studies conducted during the pilot study, it is evident that the main process units of the **ISEP+™** system performed each function effectively and efficiently. The integrated **ISEP+™** system was successful in maintaining acceptable performance level, although the period of continuous integrated operation was relatively short. A low overall brine waste stream, at ~0.16% of the feed water treated, has been obtained in the integrated **ISEP+™** system. This waste stream contains non-detectable levels of perchlorate (<125 ppb) and nitrate (<20 ppm) and so, can be easily disposed.

LIST OF FIGURES

- Figure 1. Schematic of the **ISEP+™** process implemented at JPL site.
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Appendix. Perchlorate breakthrough profile over granular activated carbon (GAC) observed during JPL pilot study.

Figure 1. Conceptual Diagram of the ISEP+ system as implemented at JPL site.

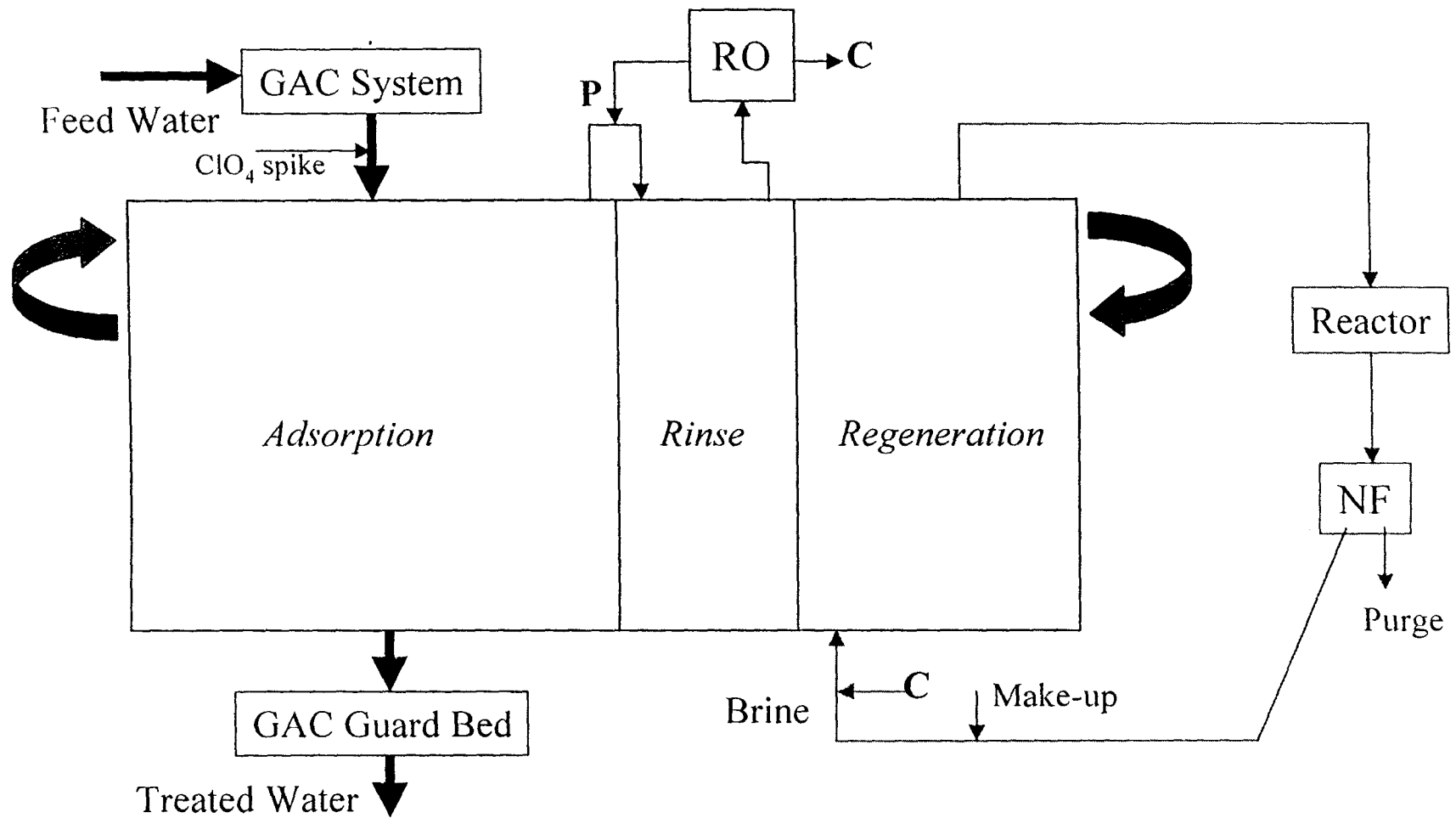


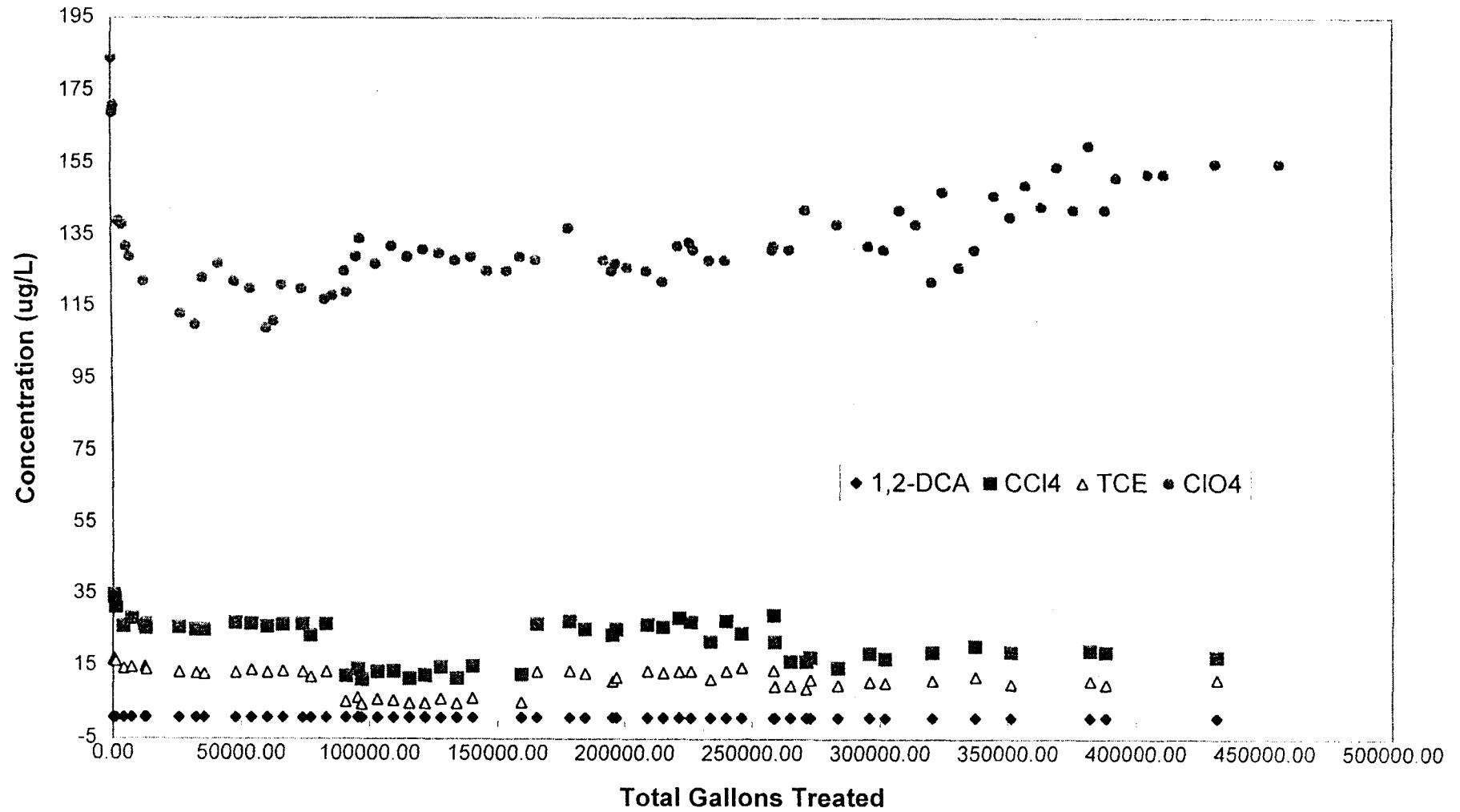
Figure 2. Representative VOC and ClO₄ Profile Data for MW-7 well at JPL

Figure 3. cis-1,2-DCA concentration data from GAC system during JPL pilot trial.

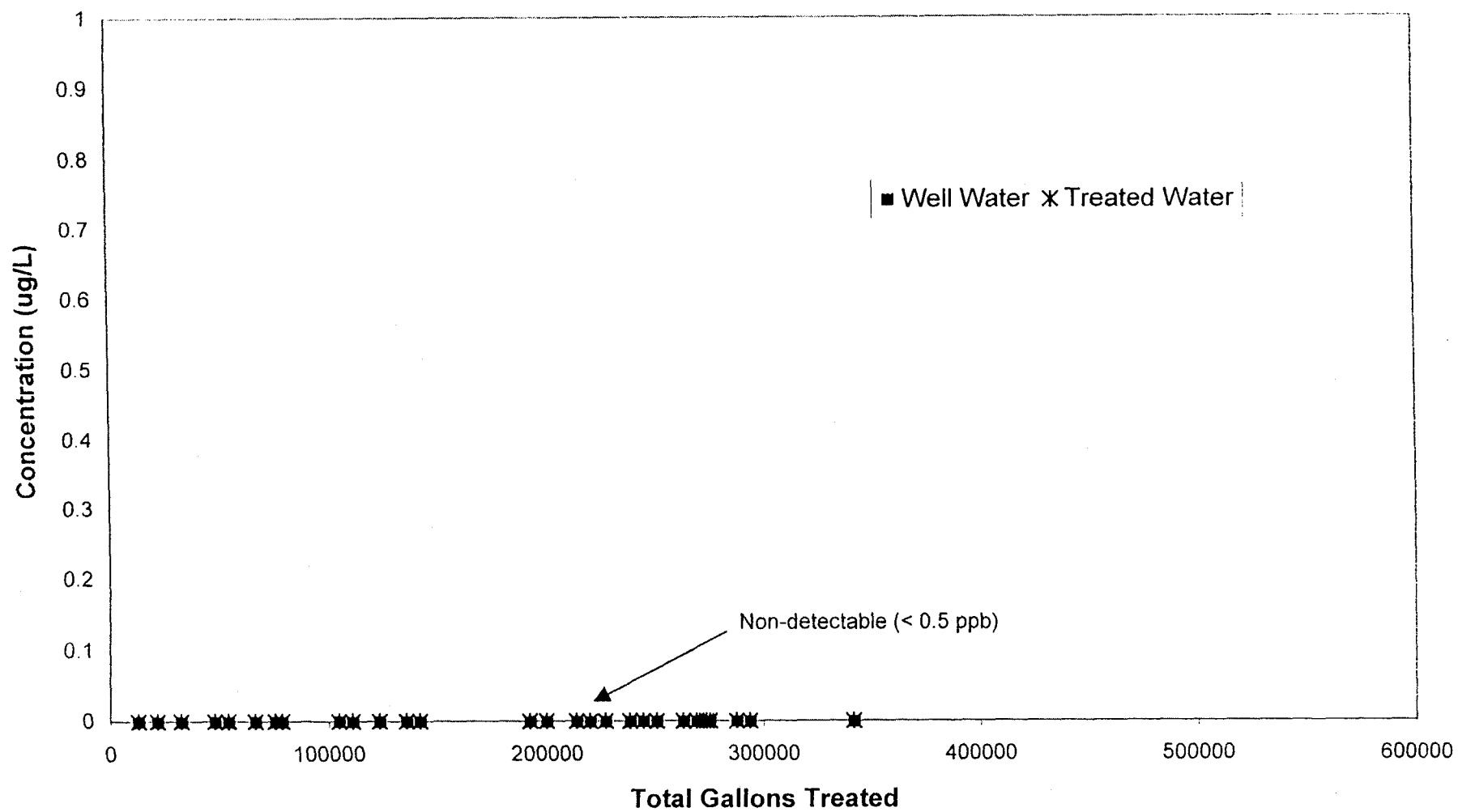


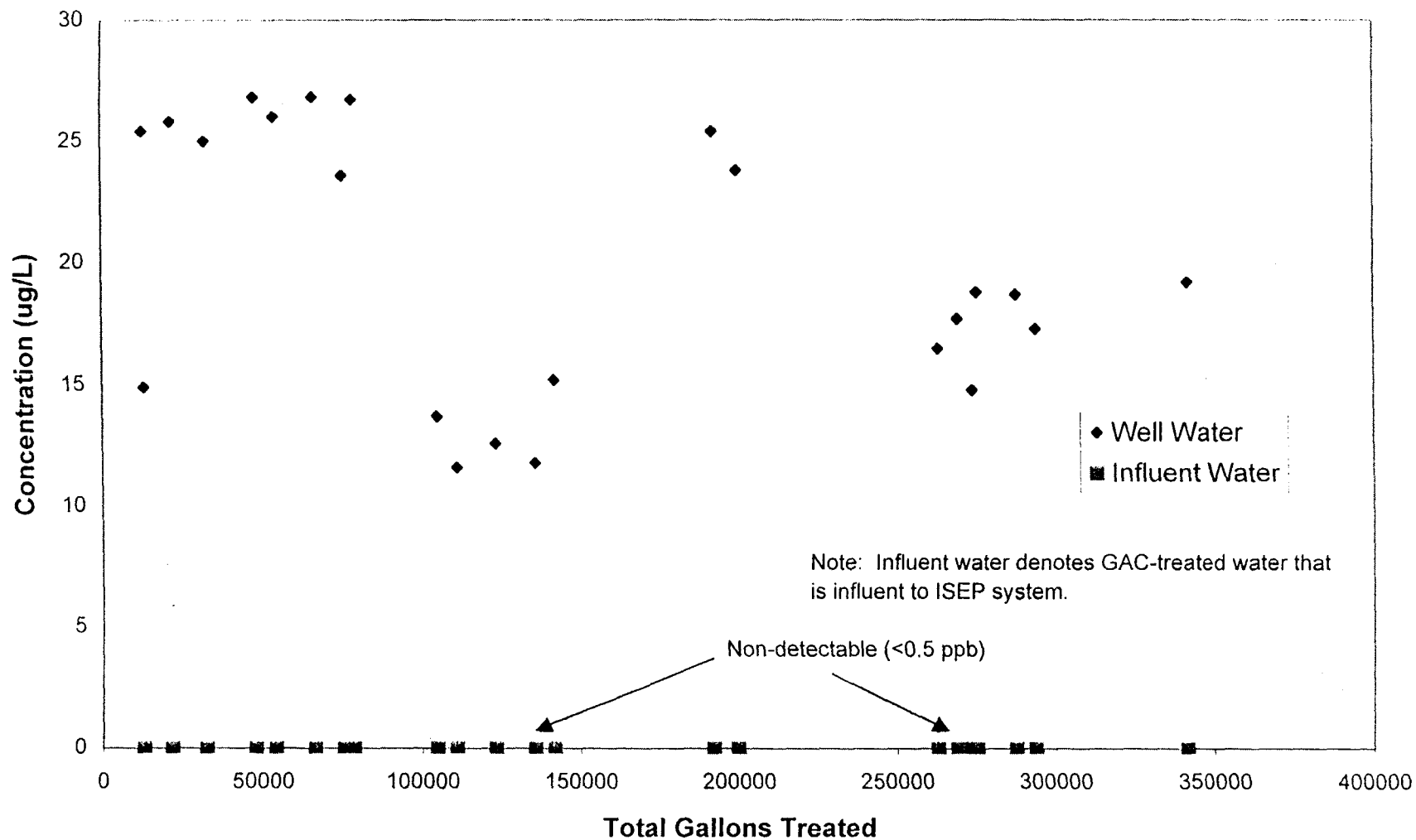
Figure 4. Representative CCl₄ removal data from GAC system during JPL pilot trial.

Figure 5. Representative TCE removal data from GAC system during JPL pilot trial

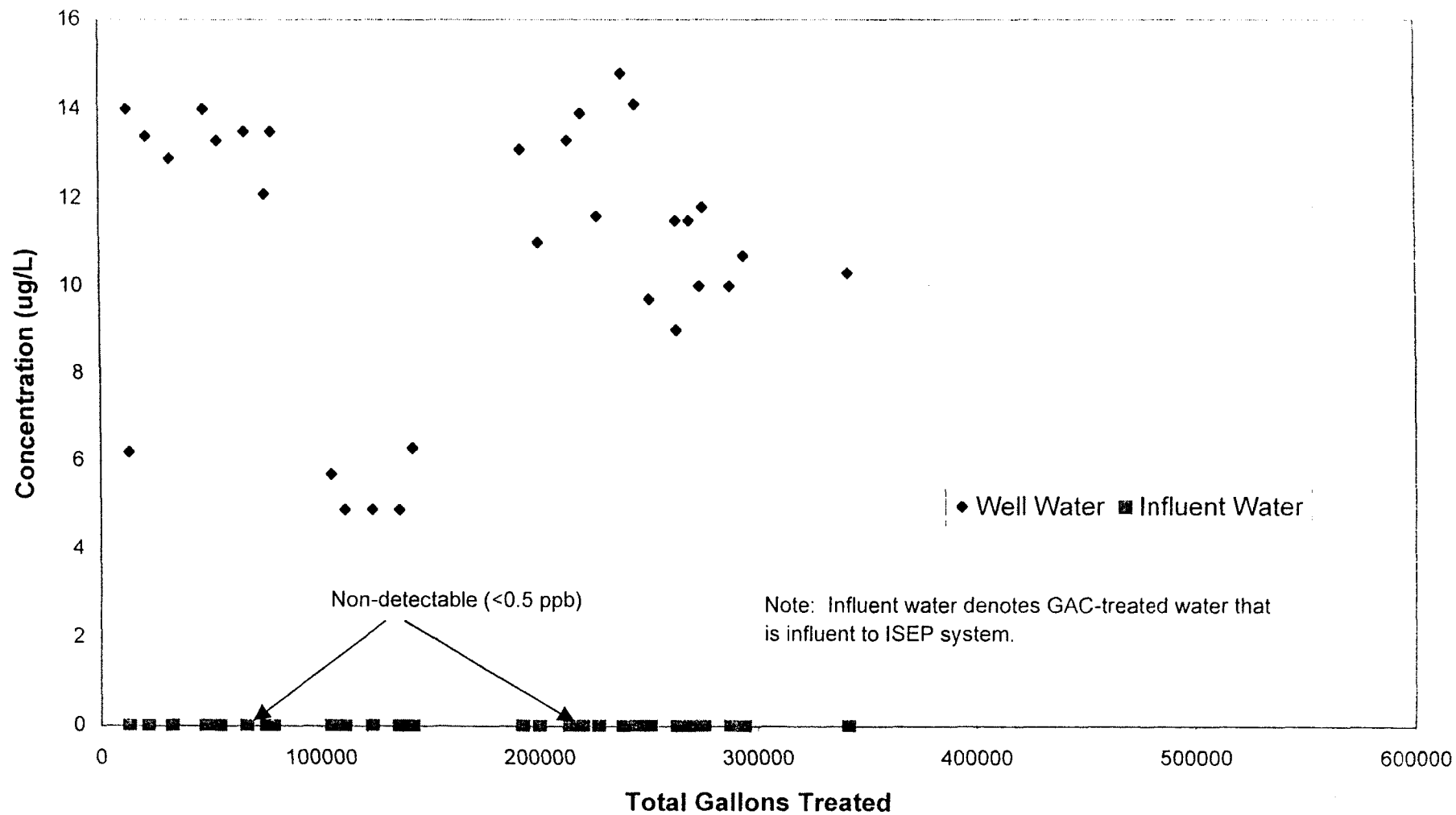


Figure 6. Perchlorate removal performance of the ISEP® system at ~250 ppb and ~1200 ppb influent concentrations.

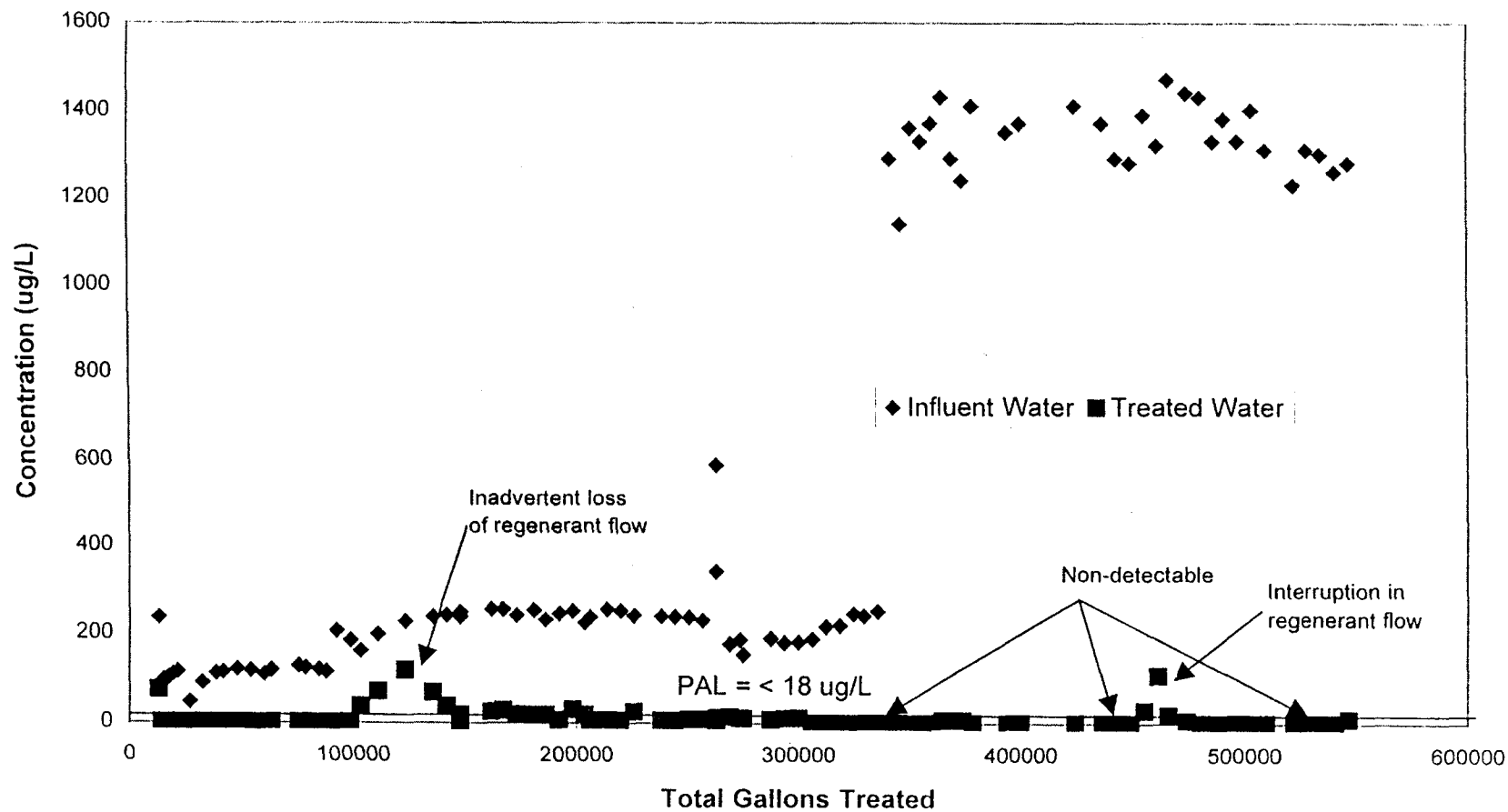


Figure 7. Nitrate removal performance of the ISEP® system during JPL pilot trial

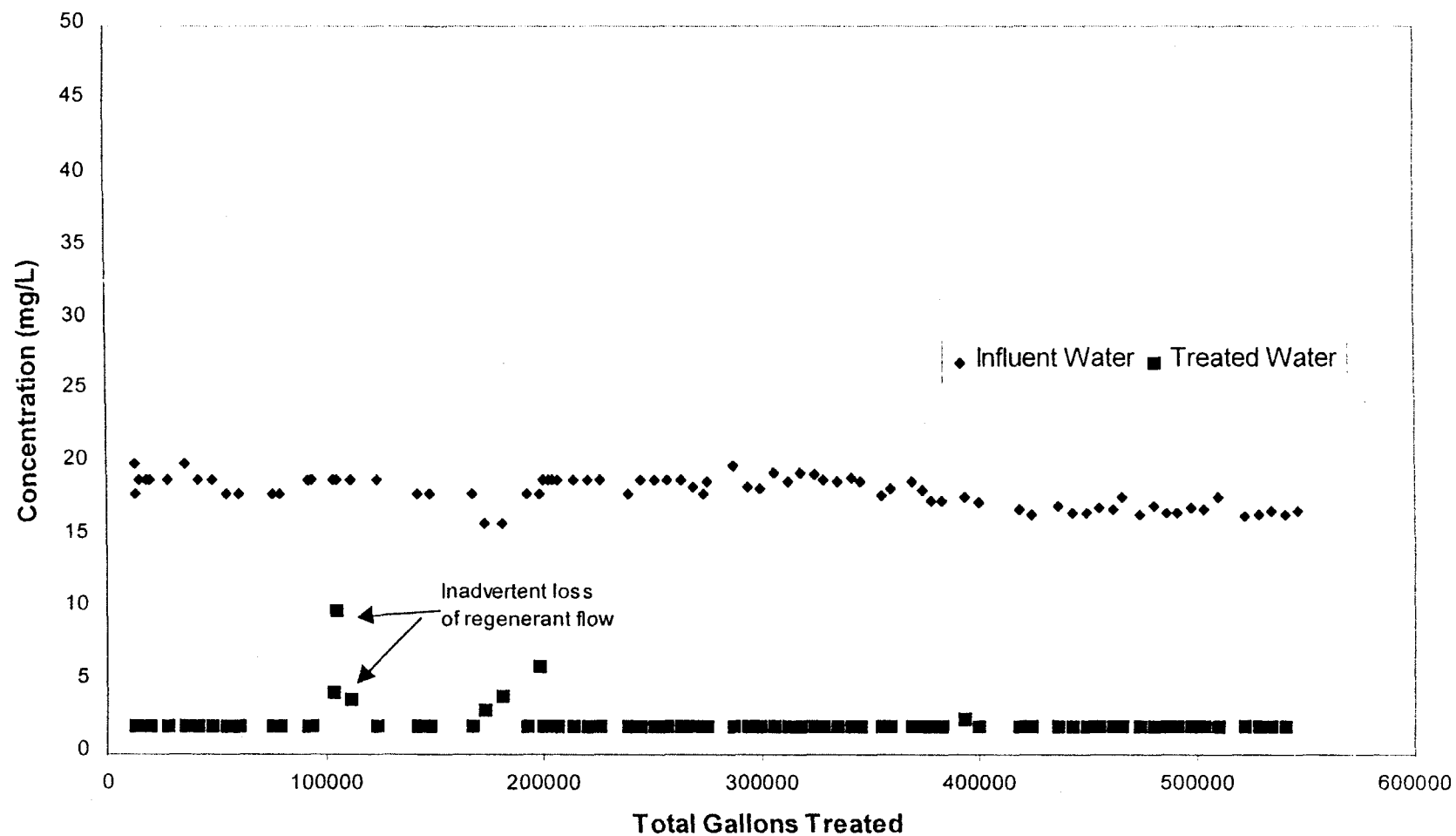


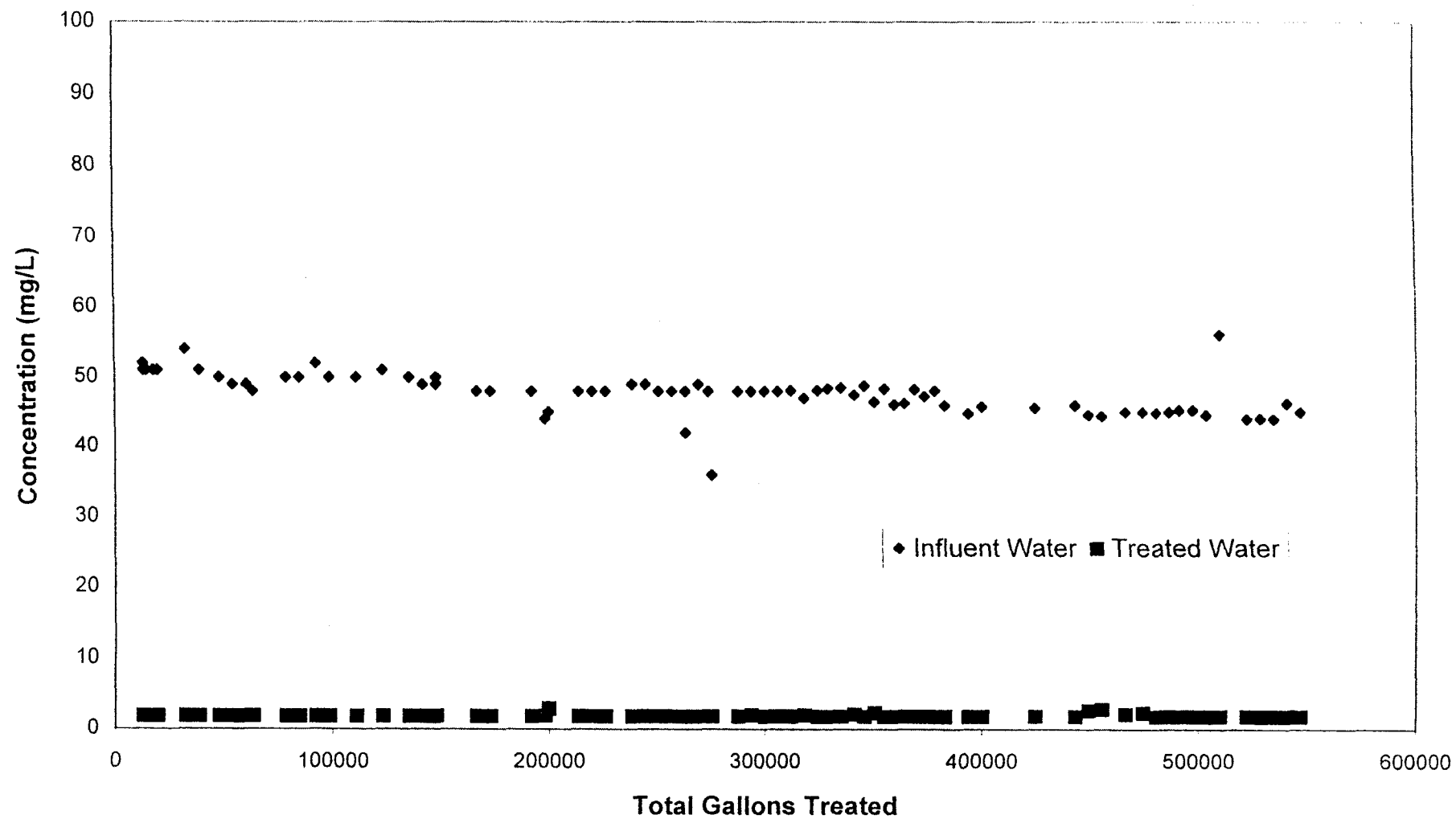
Figure 8. Sulfate removal performance of the ISEP® system during JPL pilot trial.

Figure 9. Steady state destruction of Perchlorate in PNDM during JPL pilot trial.

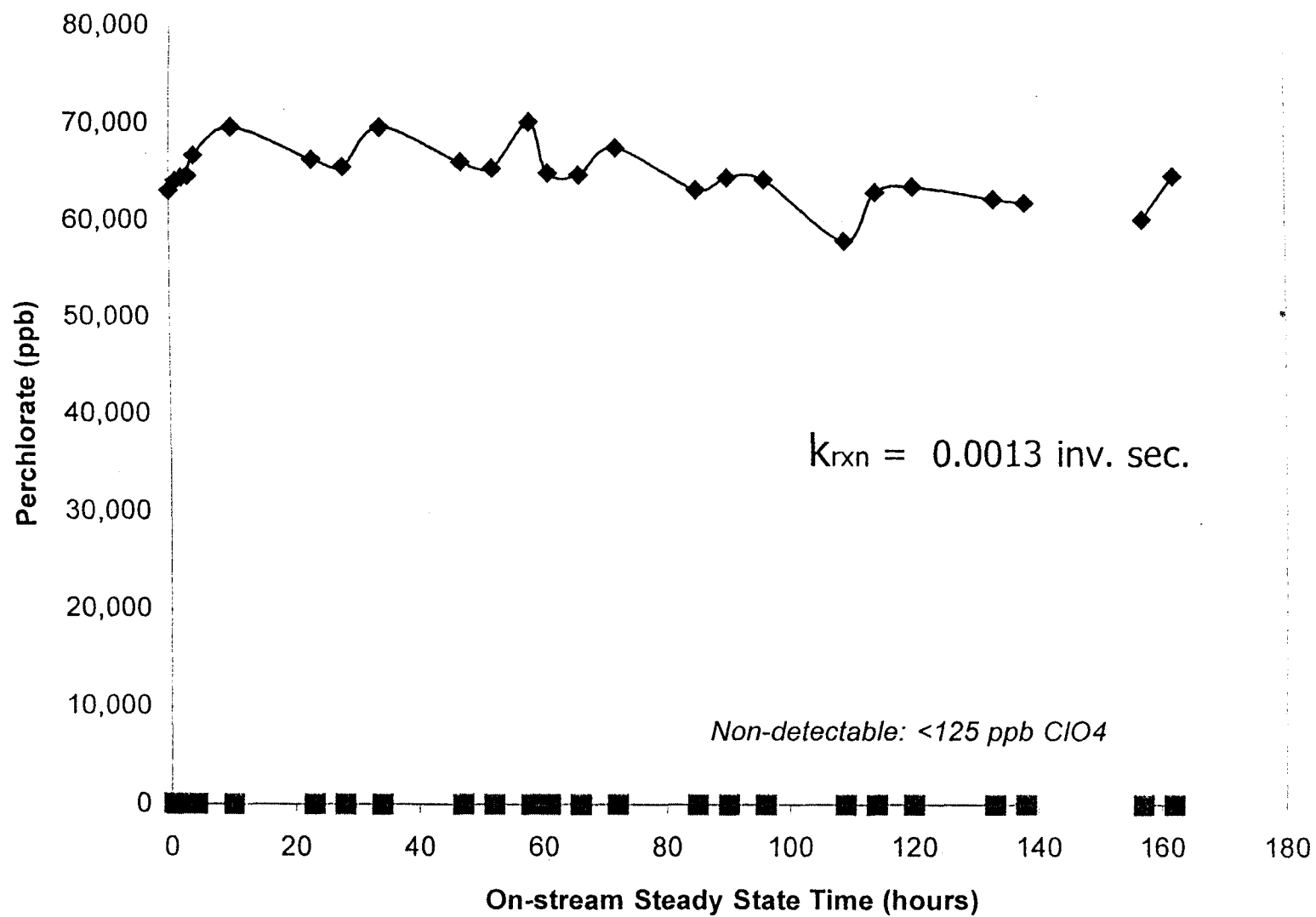


Figure 10. Steady state destruction of Nitrate in PNDM during JPL pilot trial.

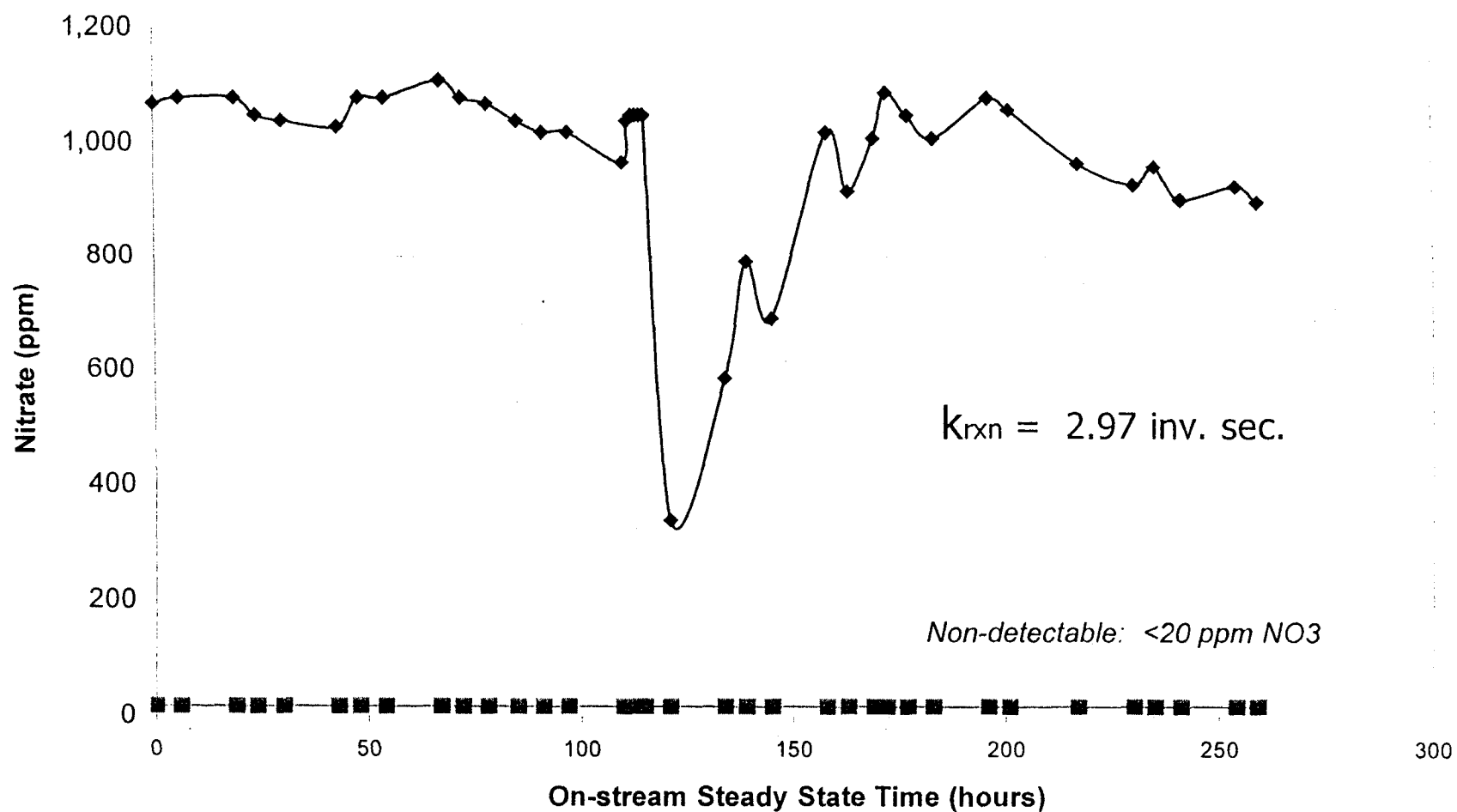


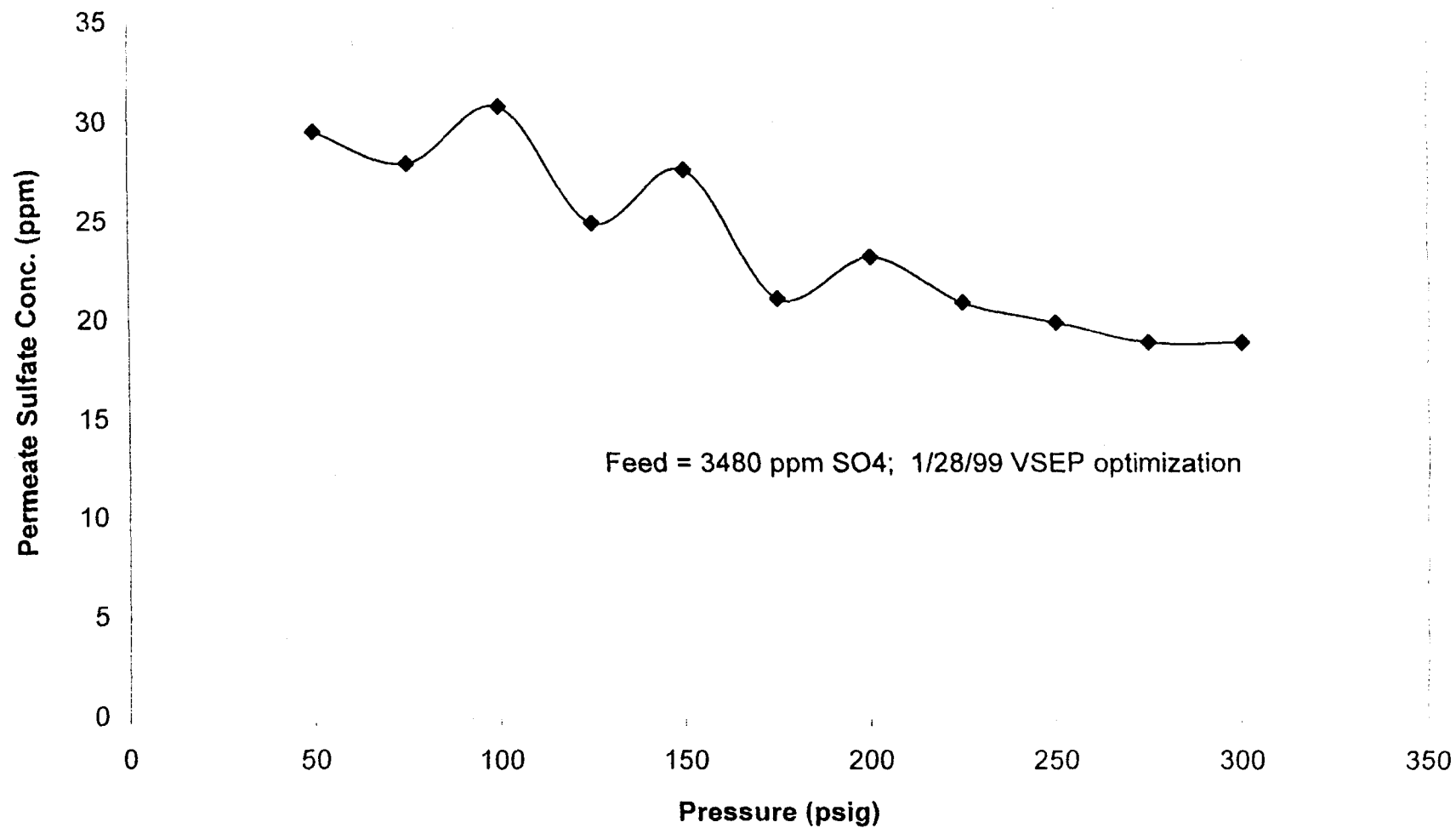
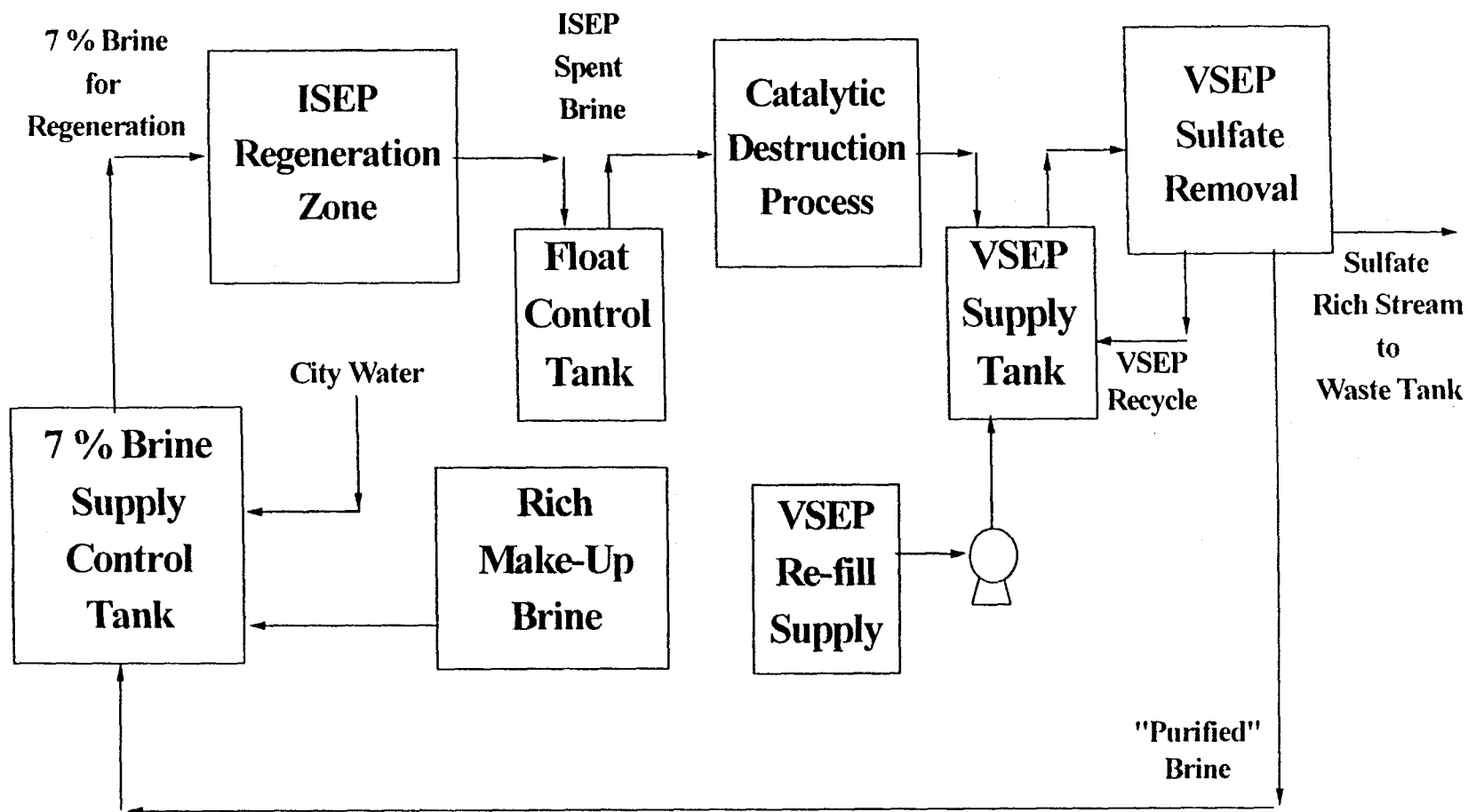
Figure 11. Impact of nanofiltration operating pressure on permeate sulfate concentration.

Figure 12. ISEP+ Integration Strategy at JPL



Appendix: Perchlorate breakthrough profile over granular activated carbon (GAC) observed during JPL Pilot Study.

Profile from GAC Bed 1 in ISEP+™ system.

